



^{13}C Solution NMR Spectra of Poly(ether)urethanes

John A. Hiltz

Defence R&D Canada

Technical Memorandum

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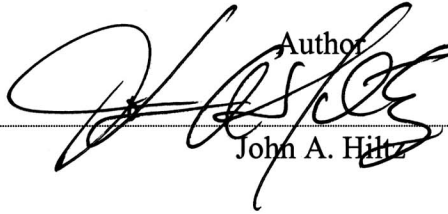
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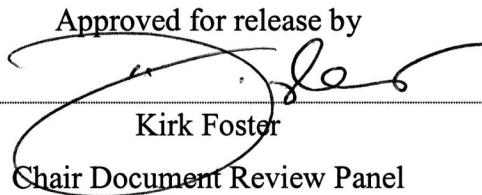
November 2002

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Abstract

The ^{13}C solution nuclear magnetic resonance (NMR) spectra of the 15 poly(ether)urethanes are presented. The poly(urethane)s were prepared using one of two diisocyanates, either methylene diphenyl diisocyanate (MDI) or hexamethylene diisocyanate (HDI), one of five poly(ether glycol)s, poly(tetramethylene ether glycol) of molecular weight 650, 1000, or 1400, or poly(ethylene glycol) of molecular weight 600 or 1000, and one of three chain extenders, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, or diethylene glycol. These polymers were prepared as part of a modelling study to determine if Group Contribution Theory and Group Interaction Modelling could be used to predict dynamic mechanical properties of poly(ether)urethanes on the basis of the structural fragments in the polymers.

The chemical shifts of the unique carbons in each of the poly(urethane)s are assigned. They can be used to unambiguously identify the diisocyanate/diol/poly(ether glycol) used to prepare the various polyurethanes. For some compounds the spectra show resonances for terminal hydroxyl substituted carbons. These could provide a method, under the right experimental conditions, to compare molecular weights of batches of the same polymer.

Résumé

On présente les spectres de résonance magnétique nucléaire (RMN) du ^{13}C de 15 poly(éther)uréthanes en solution. Ces polyuréthanes ont été préparés à partir de deux diisocyanates, soit le diisocyanate de méthylènediphényle (MDI) et le diisocyanate d'hexaméthylène (HMDI), un de cinq poly(éther glycol)s, un poly(tétraméthylène éther glycol) d'un poids moléculaire de 650, 1000 ou 1400, ou un polyéthylèneglycol d'un poids moléculaire de 600 ou 1000, et un de trois allongeurs de chaîne, soit le butane-1,4-diol, le 2,2-diméthylpropane-1,3-diol ou le diéthylèneglycol. Ces polymères ont été préparés dans le cadre d'une étude de modélisation visant à déterminer si des approches comme la Théorie de la contribution des groupes et la Modélisation des interactions de groupes permettraient de prévoir les propriétés mécaniques dynamiques des poly(éther)uréthanes à partir des fragments structuraux dans les polymères.

On a déterminé les déplacements chimiques des carbones caractéristiques dans chacun de ces polyuréthanes. Ces déplacements peuvent être utilisés pour identifier sans ambiguïté le diisocyanate/diol/poly(éther glycol) à partir desquels les divers polyuréthanes ont été préparés. Dans le cas de certains composés, les spectres indiquent qu'il y a résonance des carbones terminaux substitués par un hydroxyle. Dans des conditions expérimentales appropriées, cette résonance permettrait de comparer les poids moléculaires de lots d'un même polymère.

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Executive summary

Introduction

Thermoplastic polyurethane elastomers are segmented block copolymers whose structure and properties depend on a number of parameters including the materials used in their synthesis, the relative proportion of the starting materials, and the method used in their synthesis. It follows that by varying these parameters, polymers with a range of properties can be prepared. In the absence of relationships that correlate structure and properties, the preparation of a polymer with the desired properties for a particular application can require the synthesis and characterization of a large number of compounds.

It is therefore desirable to have modelling tools that allow the prediction of properties based on the chemistry and concentrations of the starting materials. To this end, a series of poly(ether)urethanes have been synthesized and their dynamic mechanical properties measured. The goal was to determine if modelling approaches, such as Group Interaction Modelling or Group Contribution Theory, could be used to evaluate the contributions of structural groups in this series of polymers to the observed dynamic properties. If so, then the models could be used to predict starting materials and their relative concentrations required to prepare a polymer with the required properties.

An integral part of this study was the chemical characterization of the poly(ether)urethanes prepared for the study. This is required to determine the actual structure of the synthesized polymers.

Principal results

In this memorandum, the ^{13}C solution NMR spectra of the poly(ether)urethanes prepared for modelling study are presented. Chemical shifts of the unique carbons in each of the polymers have been assigned. The chemical shifts of the unique carbons in each of the polymers can be used to identify the starting materials used in their preparation. The relative intensities of the unique carbons gives a qualitative measure of the relative concentrations of the starting materials used in its preparation.

Significance of Results

Characterization of polymeric materials is essential to establishing relationships between polymer structure and properties. A thorough understanding of these relationships is critical in developing polymers with properties tailored for various applications.

John A. Hiltz. 2002. ^{13}C Solution NMR Spectra of Poly(ether)urethanes. DRDC Atlantic TM 2002-146. Defence Research and Development Canada – Atlantic.

Sommaire

Introduction

Les élastomères thermoplastiques de polyuréthane sont des copolymères séquencés segmentés dont la structure et les propriétés dépendent d'un certain nombre de paramètres, par exemple, les matières utilisées pour leur synthèse, les proportions relatives de ces matières et la méthode de synthèse utilisée. On peut donc, en faisant varier ces paramètres, préparer des polymères présentant toute une gamme de propriétés. En l'absence de relations permettant de corréler la structure et les propriétés, il pourrait être nécessaire de synthétiser et de caractériser un grand nombre de composés avant d'obtenir un polymère présentant les propriétés recherchées en vue d'une application particulière.

Il est donc souhaitable de disposer des outils de modélisation permettant de prévoir les propriétés d'un polymère à partir de la composition chimique des matières de départ et de leurs proportions. C'est dans ce but que nous avons synthétisé une série de poly(éther)uréthanes, puis mesuré leurs propriétés mécaniques dynamiques. L'objectif était de déterminer si des approches de modélisation, comme la Modélisation des interactions de groupes ou la Théorie de la contribution des groupes, pouvaient être utilisées pour évaluer dans quelle mesure les groupes structuraux dans cette série de polymères contribuaient aux propriétés dynamiques observées. Dans un tel cas, ces modèles pourraient être utilisés pour déterminer les matières de départ à utiliser, ainsi que leurs proportions relatives, pour préparer un polymère présentant les propriétés recherchées.

La caractérisation chimique des poly(éther)uréthanes préparés faisait partie intégrante de la présente étude. Elle s'est avérée indispensable pour déterminer la structure réelle des polymères synthétisés.

Principaux résultats

Dans le présent exposé, on présente les spectres RMN du ^{13}C des poly(éther)uréthanes en solution préparés pour l'étude de modélisation. On a déterminé les déplacements chimiques des carbones caractéristiques dans chacun des polymères. Ces déplacements peuvent servir à identifier les matières de départ utilisées pour la synthèse. Les intensités relatives des carbones caractéristiques donnent une mesure qualitative des concentrations relatives des matières de départ ayant servi à la préparation des polymères.

Importance des résultats

La caractérisation des matières polymériques est essentielle à l'établissement de relations liant la structure du polymère et ses propriétés. Une compréhension approfondie de ces relations est indispensable à la préparation de polymères présentant les propriétés recherchées pour diverses applications.

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1. Introduction

Thermoplastic poly(urethane) (TPU) elastomers are synthesized from a diisocyanate, a poly(ester glycol) or poly(ether glycol), and a chain extender such as 1,4-butanediol or 2,2-dimethyl-1,3-propanediol. These elastomers are segmented block copolymers consisting of urethane rich hard segments and poly(ester glycol) or poly(ether glycol) rich soft segments. The structure and therefore the properties of these compounds depend on a number of parameters. These include the nature of the diisocyanate, polyol, and chain extender, the relative proportion of hard and soft segments, the molecular weight of the poly(ester glycol) or poly(ether glycol), and the method, for instance, a one or a two step synthesis, used to prepare the polymer [1-3].

By changing the nature of the constituent chemicals and their relative concentrations, properties such as the glass transition temperature (T_g), can be varied significantly. It follows that by the selection of the starting materials and their relative concentrations, polymers can be synthesized that have the required properties for a particular application. In the absence of relationships that correlate structure and properties, a wide range of compounds must be synthesized and characterized to determine which one has the required properties. Obviously, it would be desirable to have modelling tools that would allow one to predict properties based on the chemistry and relative concentrations of the starting materials. To this end, a series of poly(ether)urethanes were synthesized and characterized. Group Contribution Theory and Group Interactive Modelling were used in an attempt to evaluate the contribution of poly(ether)urethane structural groups to the observed dynamic mechanical properties of the polymer [4,5].

Characterization of the poly(ether)urethanes included dynamic mechanical analysis, differential scanning calorimetry, infrared spectroscopy, pyrolysis gas chromatography and ^{13}C solution nuclear magnetic resonance (NMR) spectroscopy. These characterization techniques probed the structure, the dynamic response and thermal properties of the poly(ether)urethanes.

In this memorandum, the ^{13}C solution nuclear magnetic resonance (NMR) spectra of the 15 poly(ether)urethanes used in the modelling study are presented. The poly(urethane)s were prepared using one of two diisocyanates, one of five poly(ether glycol)s, and one of three chain extenders. The diisocyanates were methylene diphenyl diisocyanate (MDI) or hexamethylene diisocyanate (HDI), the poly(ether glycol)s were poly(tetramethylene ether glycol) of molecular weight 650, 1000, or 1400, or poly(ethylene glycol) of molecular weight 600 or 1000 and the diols were 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, or diethylene glycol.

2. Experimental

2.1 Materials

The polyurethanes were synthesized by Bodycote, Mississauga, Ontario [6]. All syntheses were carried out in dimethylformamide.

The 19 polyurethane samples are listed in Table 1. Four samples DREA1R, DREA9R, DREA13R, and DREA16R are repeat synthesis of samples DREA1, DREA9, DREA13, and DREA16, respectively. The structures of the reactants used to prepare the samples are shown in Figure 1. The poly(urethane)s were prepared using one of two diisocyanates, 4,4'-methylenabis(phenyl isocyanate) (MDI) or 1,6-diisocyanatohexane (HDI); one of three diols, 1,4-butanediol (BDO), diethylene glycol (DEG), or 2,2-dimethyl-1,3-propanediol (DMPD); and one of two polyols, poly(tetramethylene ether glycol) or poly(ethylene glycol). The poly(tetramethylene ether glycol)s had molecular weights of 650 (T650), 1000 (T1000), and 1400 (T1400). The poly(ethylene glycol)s had molecular weights of 600 (P600) and 1000 (P1000). Two of the samples (DREA1 and DREA13) were synthesized using only a diisocyanate and a diol and one sample (DREA16) from a diisocyanate and a poly(tetramethylene ether glycol). These samples are not block copolymers; samples DREA1 and DREA13 contain only hard segments and sample DREA16 only soft segments.

2.2 Nuclear Magnetic Resonance Spectroscopy

Solution ^{13}C NMR spectra were acquired on a Bruker AMX-400 (100.62 MHz for ^{13}C) NMR spectrometer at the Atlantic Region Magnetic Resonance Centre, Dalhousie University, Halifax, Nova Scotia. All samples were run in a 5 mm probe as solutions in dimethylformamide (Fisher Scientific, ACS grade). The percent polymer (weight/weight) in each of the solutions is shown in Table 1. Typically 1000 scans were acquired using composite pulse decoupling. The pulse width was 2.4 μs , the relaxation delay 1.0 s, and the acquisition time was 0.54 s (16K real data points over a sweep width of 30.488 kHz).

J-Mod spectra were also acquired for the poly(ether)urethanes. The NMR conditions were the same except that the pulse width was 7.3 μs and an evolution delay of 6.9 ms was used within the echo. In the J-Mod or attached proton test (APT) experiment carbons with 1 or 3 attached protons can be distinguished from carbons with 0 or 2 attached protons. That is, carbons with 1 or 3 protons give a positive response while carbons with 0 or 2 protons give a negative response. This information is useful in assigning the resonance frequencies of the carbons in the NMR spectra.

Simulated ^{13}C NMR spectra were calculated using ^{13}C NMR Predictor Version 4.5 (Advanced Chemistry Development Laboratory).

Table 1. Molar ratios of reactants used to prepare poly(ether)urethane samples DREA1 to DREA18. The structures of the reactants are shown in Figure 1.

	BDO	T650	T1000	T1400	DEG	P600	P1000	DMPD	MDI	HDI	WT %
1	1								1		11.2
1R	1								1		12.9
3			1					0.5	1.5		12.9
4			1					5	6		12.1
5				1				1	2		11.9
6				1				5	6		9.3
7					1			1		2	10.3
8						1		0.5	1.5		9.5
9							1	1	2		12.1
9R							1	1	2		13.6
10							1	5	6		10.8
11							1	5		6	11.4
13					1				1		12.8
13R					1				1		12.9
14		1						5	6		11.2
16			1						1		8.9
16R			1						1		9.8
17			1					3	4		13.7
18			1					3		4	14.5

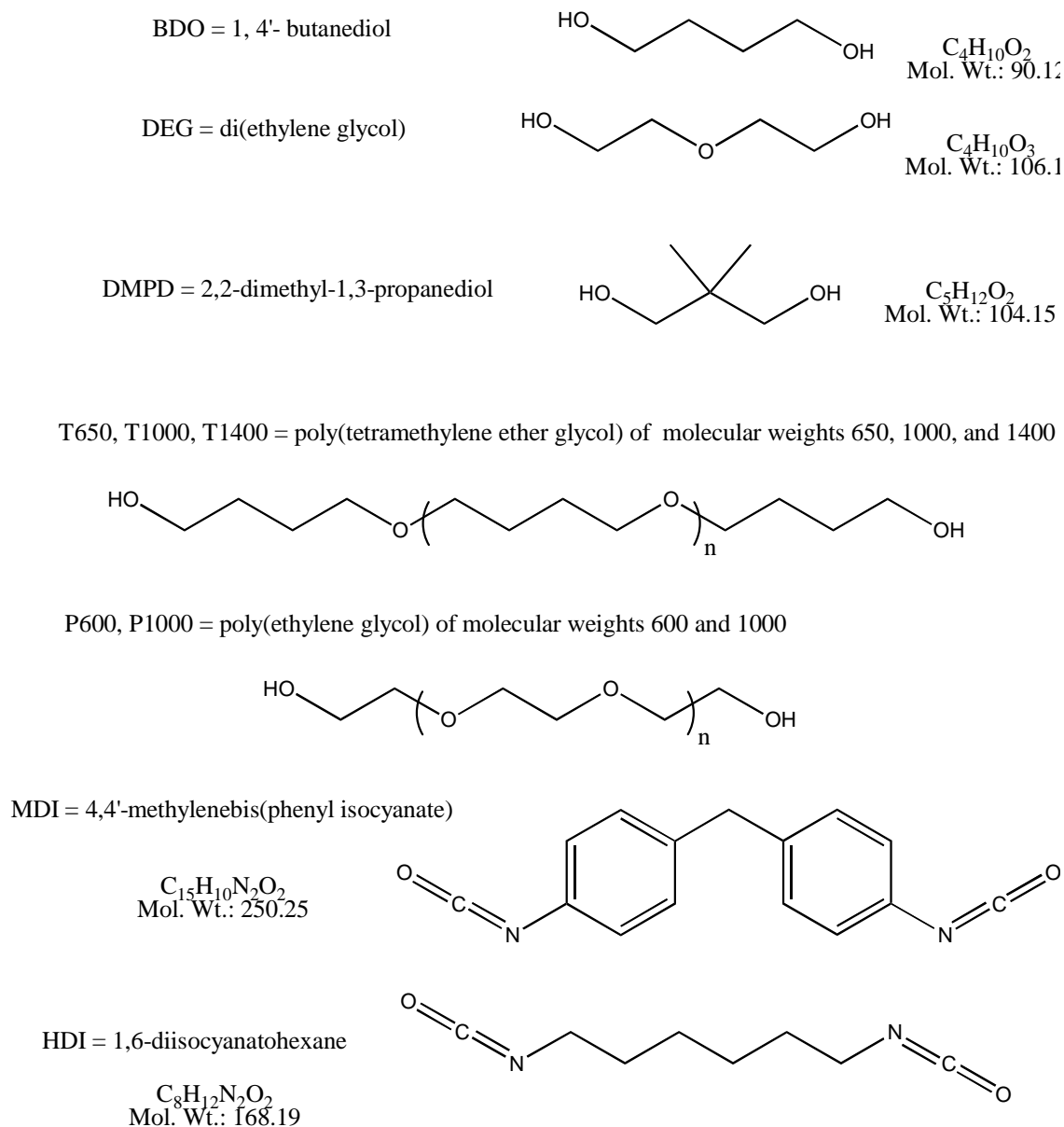


Figure 1. Structure of the reactants used to prepare polyurethane samples DREA1 to DREA18.

3. Results and Discussion

The spectra of the MDI based and HDI based poly(urethane)s will be discussed separately. The resonances at 31.08 ppm, 36.19 ppm, and 162.98 ppm in the NMR spectra arise from the dimethylformamide carbons.

3.1 MDI Based Poly(urethane)s

3.1.1 DREA1 and DREA1R- MDI/BDO (1/1)

The NMR spectra of samples DREA1 and DREA1R are shown in Figures 2 and 3 respectively. They were synthesized from MDI/BDO (1/1) and as they contain no poly(ether glycol) are composed of hard segments (urethane rich phase) only. The structure of a repeat unit of the polymer is shown in Figure 4.

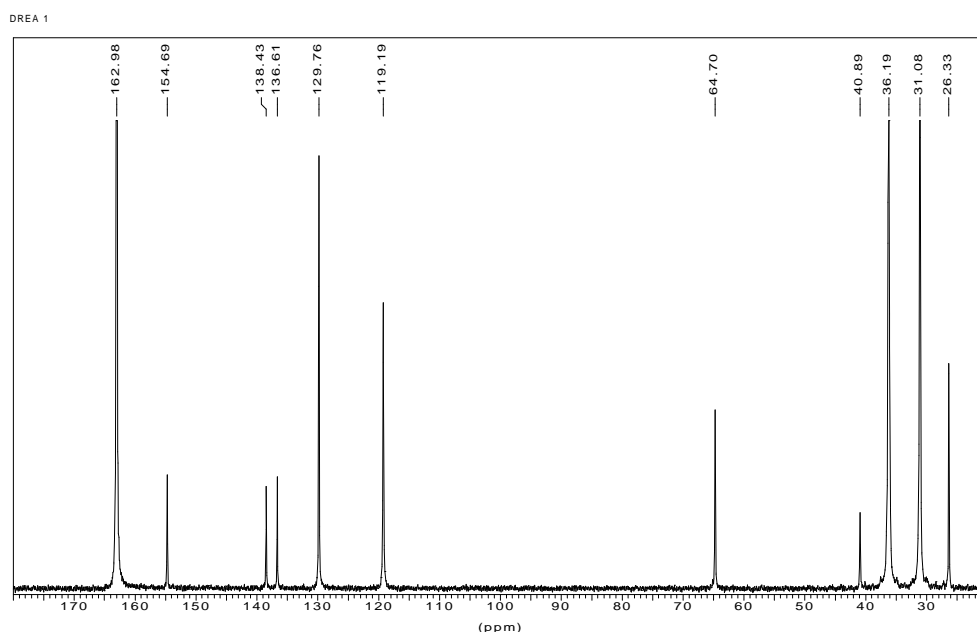


Figure 2. Proton decoupled ^{13}C solution NMR spectra of DREA1 poly(urethane) - MDI/BDO (1/1).

The assignment of the resonances for the unique carbons atoms, i.e., those numbered C_1 to C_8 in Figure 4, are given in Tables 2 and 3. The assignments were made on the basis of chemical shifts of poly(urethane)s published in the literature and from simulated spectra.

The spectrum of DREA1R has resonances at 30.02 ppm and 61.77 ppm that are not present in the spectrum of DREA1. A simulated spectrum of 1,4-butanediol indicated that the chemical

shifts of the carbons one bond removed and directly attached to the hydroxyl group were 30.00 ppm and 62.70 ppm respectively. This suggests one of two things; either the sample contains unreacted 1,4-butanediol or there are more terminal OH groups per unit mass of polymer indicating that the molecular weight of DREA1R is lower than DREA1.

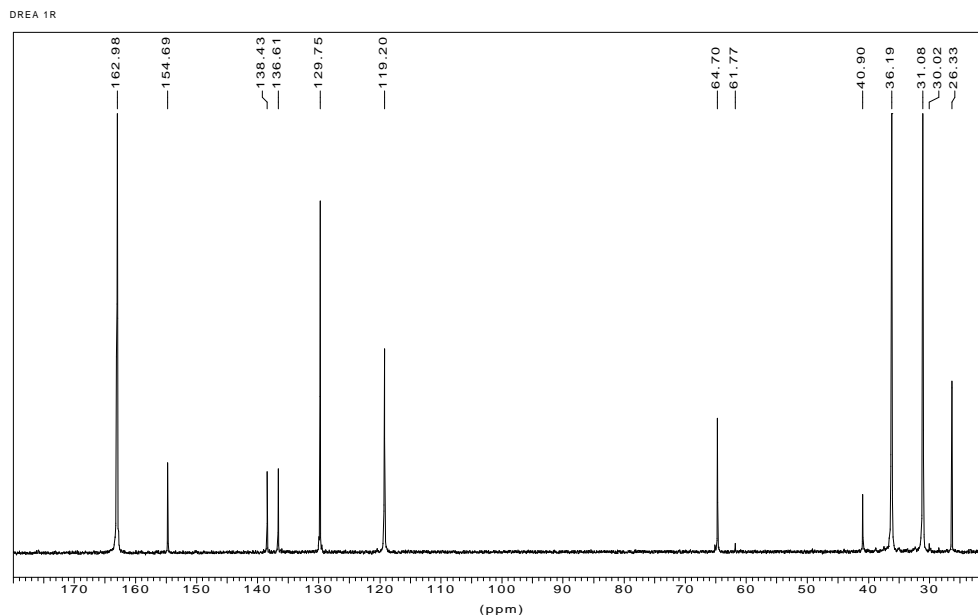


Figure 3. Proton decoupled ^{13}C solution NMR spectra of DREA1R poly(urethane) - MDI/BDO (1/1).

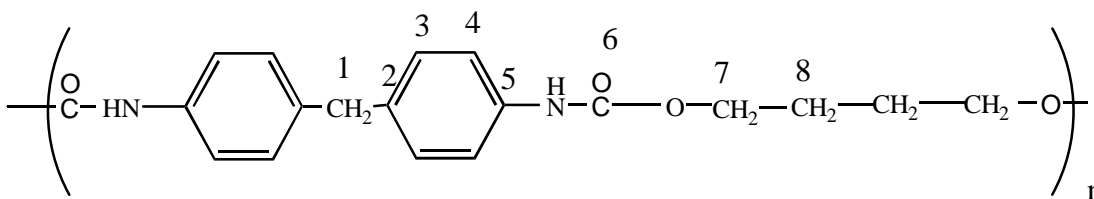


Figure 4. Structure of MDI/BDO (1/1) poly(urethane). Numbers refer to unique carbons in this polymer.

The J-Mod spectrum for DREA1 is shown in Figure 5. Referring to the structure shown in Figure 4, Carbons C_1 (40.89 ppm), C_2 (136.61 ppm), C_5 (138.43 ppm), C_6 (154.69 ppm), C_7 (64.70 ppm) and C_8 (26.33) have a negative phase. This is indicative of quaternary (0 protons attached) or methylene carbons (2 protons attached). Carbons C_3 (129.76 ppm) and C_4 (119.19 ppm) have a positive phase. This is indicative of methine carbons (1 proton attached).

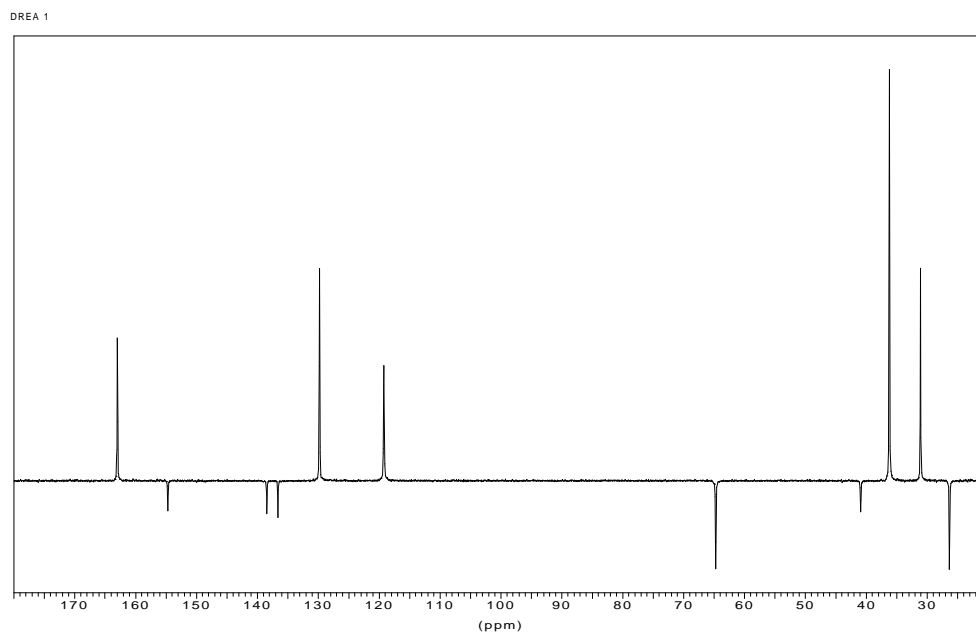


Figure 5. JMOD spectrum of DREA1. Carbons with 1 or 3 protons are positive while the carbons with 0 or 2 protons are negative.

3.1.2 DREA3- MDI/T1000/DMPD (1.5/1.0/0.5)

The spectrum of DREA3 is shown in Figure 6. The structures of the hard and soft segments of this polymer are shown in Figure 7 along with the assignment of the unique carbons. The chemical shifts of the unique carbons, i.e., those numbered in Figure 7, are listed in Tables 2 and 3.

The chemical shifts of the carbons from the MDI portion of the polymer, carbons C₁ to C₆ respectively, are similar to those for DREA1. However, this poly(urethane) contains T1000, a poly(tetramethylene ether glycol) and a different diol, 2,2-dimethyl-1,3-propanediol (DMPD), than DREA1.

The resonances at 64.97 ppm (C₉), 26.75 ppm (C₁₀), 27.00 ppm (C₁₁), 70.76 ppm (C₁₂) 71.02 ppm (C₁₃) and 27.36 (C₁₄) arise from the poly(ether glycol) portion of the polymer.

The resonances at 69.87 ppm and 21.77 ppm arise from the DMPD portion of the polymer and are assigned to carbons C₁₅ and C₁₇ respectively. No resonance was observed for carbon C₁₆. This is most likely due to the fact that it is a quaternary carbon and the small amount of diol used in the preparation of this poly(urethane). There is also a resonance at 68.20 ppm that may be due to a terminal DMPD hydroxyl substituted carbon. This is carbon C₁₈ in Table 3.

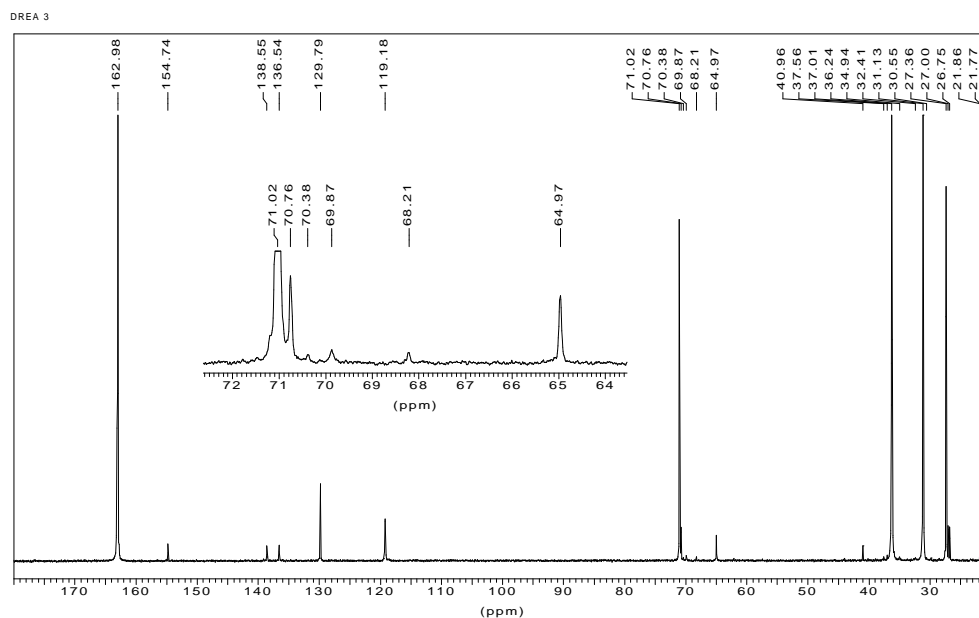


Figure 6. Proton decoupled ^{13}C solution NMR spectra of DREA3 – MDI/T1000/DMPD (1.5/1.0/0.5).

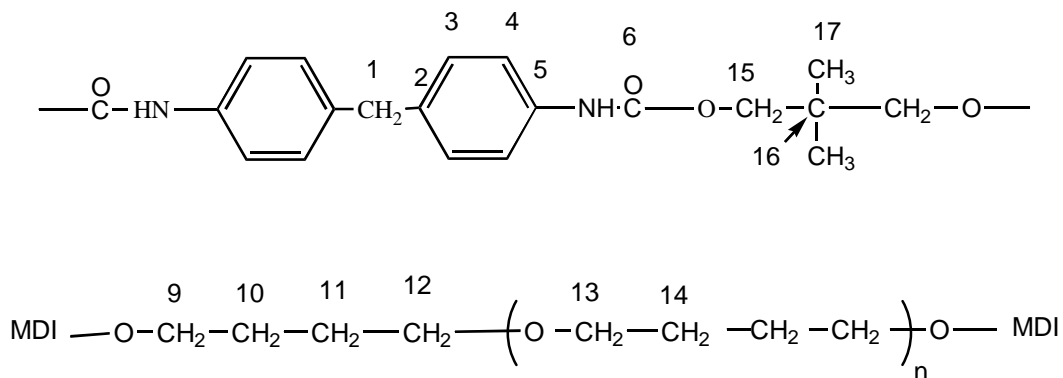


Figure 7. Structure and assignments of unique carbons in the hard (top) and soft (bottom) segments of poly(urethane)s DREA3, DREA4, DREA5, DREA6, DREA14, DREA16, and DREA17.

3.1.3 DREA4- MDI/T1000/DMPD (6/1/5)

The spectrum of DREA4 is shown in Figure 8. This polymer was prepared from the same starting materials as DREA3 but the ratios of the starting materials are different. The structures of the hard and soft segments of this polymer are shown in Figure 7 along with the assignment of the unique carbons. The chemical shifts of carbons C₁ through C₁₈ are listed in Tables 2 and 3.

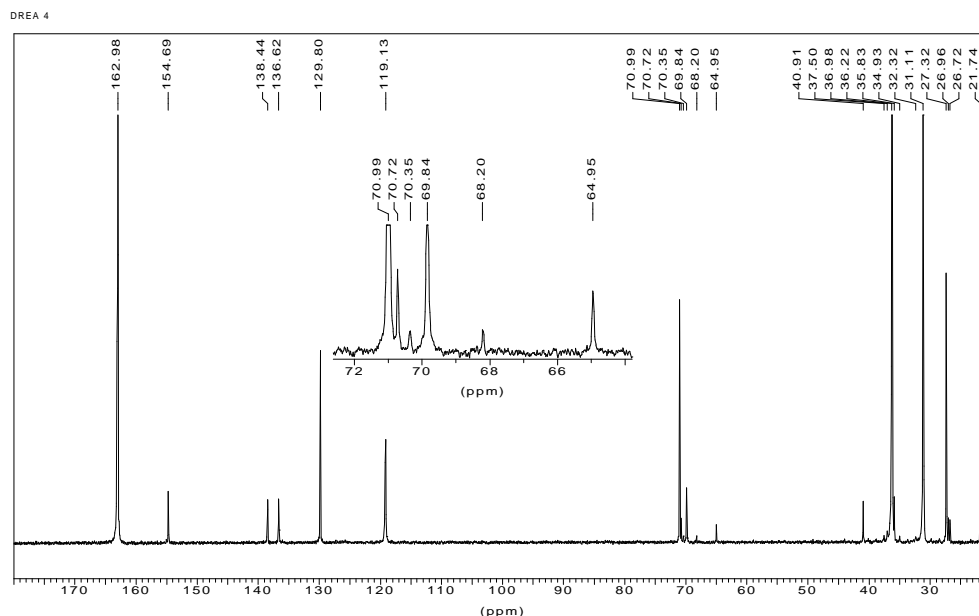


Figure 8. Proton decoupled ¹³C solution NMR spectrum of DREA4 – MDI/T1000/DMPD (6.0/1.0/5.0).

In contrast to DREA3, the resonance for carbon C₁₆ can be observed at 35.83 ppm. This resonance is somewhat difficult to see in Figure 8 because of its proximity to a resonance arising from one of the DMF methyl carbons. However, these resonances are easily distinguished in the J-Mod spectrum shown in Figure 9. The DMF methyl carbon resonance at 36.22 ppm has a positive phase while the C₁₆ quaternary carbon resonance at 35.83 ppm has a negative phase.

3.1.4 DREA5 – MDI/T1400/DMPD (2/1/1)

The spectrum of DREA5 is shown in Figure 10. The structures of the hard and soft segments of this polymer are shown in Figure 7 along with the assignment of carbon atoms in this polymer. The carbon chemical shifts are listed in Tables 2 and 3. The chemical shifts of carbons C₁ through C₁₈ are similar to those for samples DREA3 and DREA4. This is not unexpected as the starting materials for the three poly(urethane)s, with the exception of the molecular weight of the poly(ether glycol), are the same. Only the ratios of the reactants vary. The resonance for C₁₈ (terminal DMPD hydroxyl substituted carbon) is not observed in the

spectrum. This may be due to the reduced amount of DMPD used in the synthesis of this polymer.

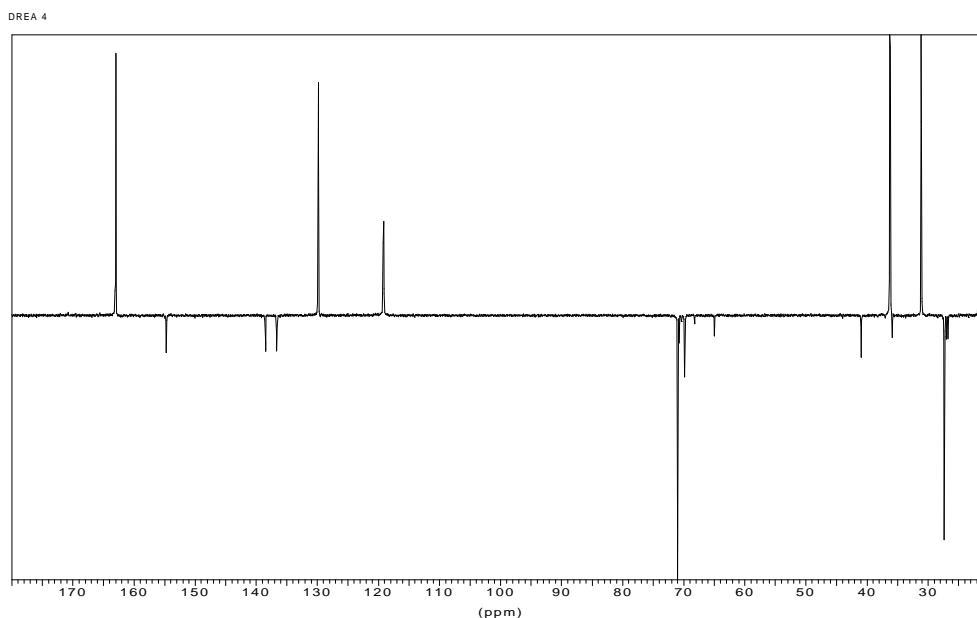


Figure 9. J-Mod spectrum of DREA4 – MDI/T1000/DMPD (6.0/1.0/5.0).

3.1.5 DREA6 – MDI/T1400/DMPD (6/1/5)

The spectrum of DREA6 is shown in Figure 11. The structures of the hard and soft segments of this polymer are shown in Figure 7 along with the assignment of the unique carbons in this polymer. The carbon chemical shifts are listed in Tables 2 and 3 and are similar to those for DREA3, DREA4, and DREA5. As the starting materials for these poly(urethane)s are the same, but the ratios of the starting materials are different, this is reflected in the relative intensities of the carbon resonances.

3.1.6 DREA8 – MDI/P600/DMPD (1.5/1.0/0.5)

The spectrum of DREA8 is shown in Figure 12. This polymer differs from those discussed in the previous section in that the poly(ether glycol) is a poly(ethylene glycol). The hard and soft segments of this polymer and the assignment of unique carbons are shown in Figure 13. The carbon chemical shifts are listed in Tables 2 and 4. The chemical shifts of the carbons in the hard segment of this polymer are the same as observed for samples DREA3 through DREA6. This is not unexpected as the diisocyanate and diol used to prepare these polymers are the same. However, no resonance for carbon C₁₆ was observed in the spectrum. This carbon was also difficult to observe in the J-Mod spectrum.

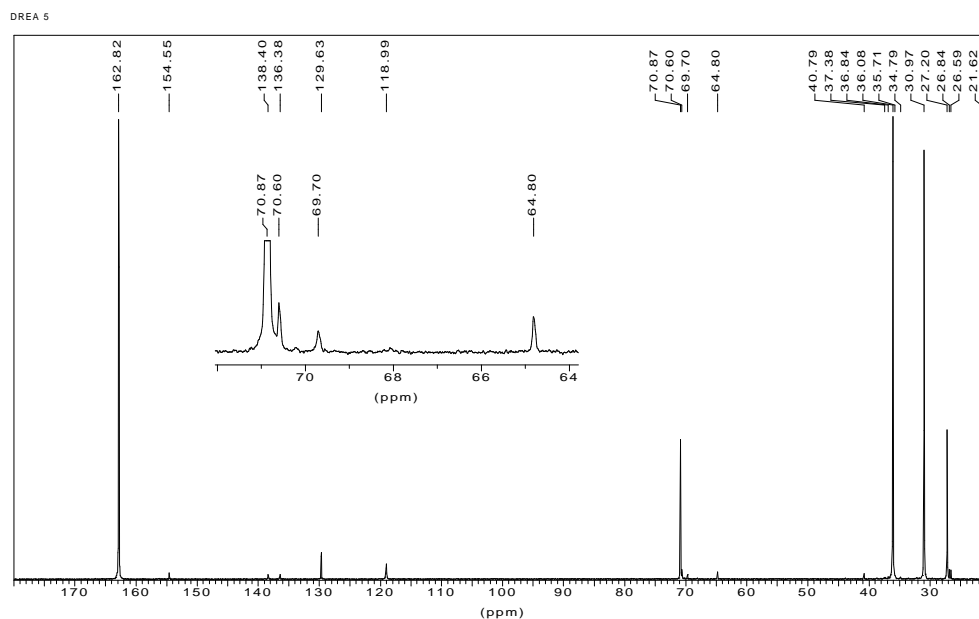


Figure 10. Proton decoupled ^{13}C solution NMR spectrum of DREA5 – MDI/T1400/DMPD (2.0/1.0/1.0).

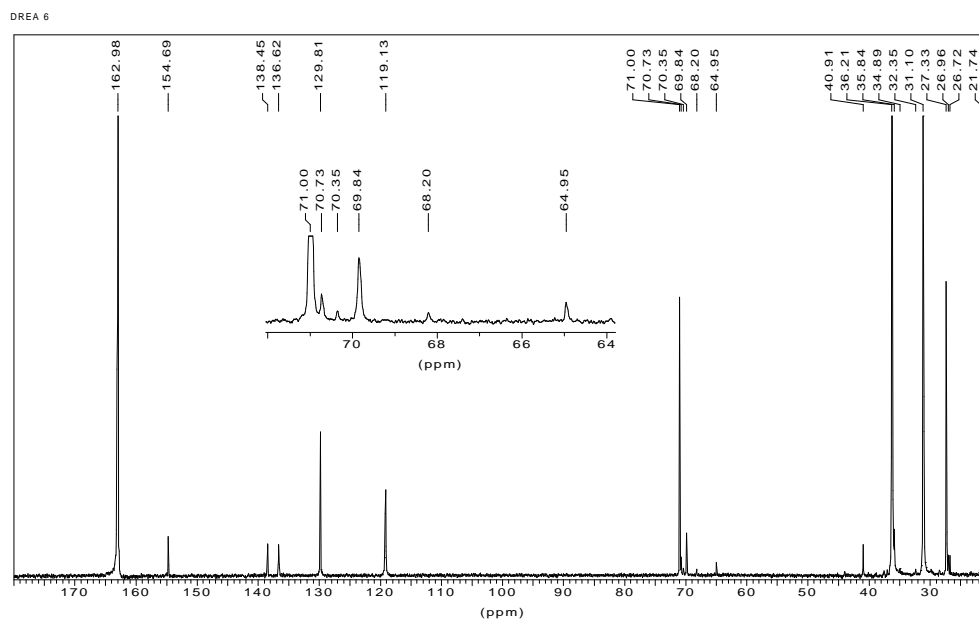


Figure 11. Proton decoupled ^{13}C solution NMR spectrum of DREA6 – MDI/T1400/DMPD (6.0/1.0/5.0).

The chemical shifts of the carbons C₁₉ (64.48 ppm) and C₂₀ (71.05 ppm) in the poly(ethylene glycol) portion of the polymer are similar to those for carbons C₉ (~65 ppm) and C₁₃ (~71 ppm) in the poly(tetramethylene ether glycol) based poly(urethane)s.

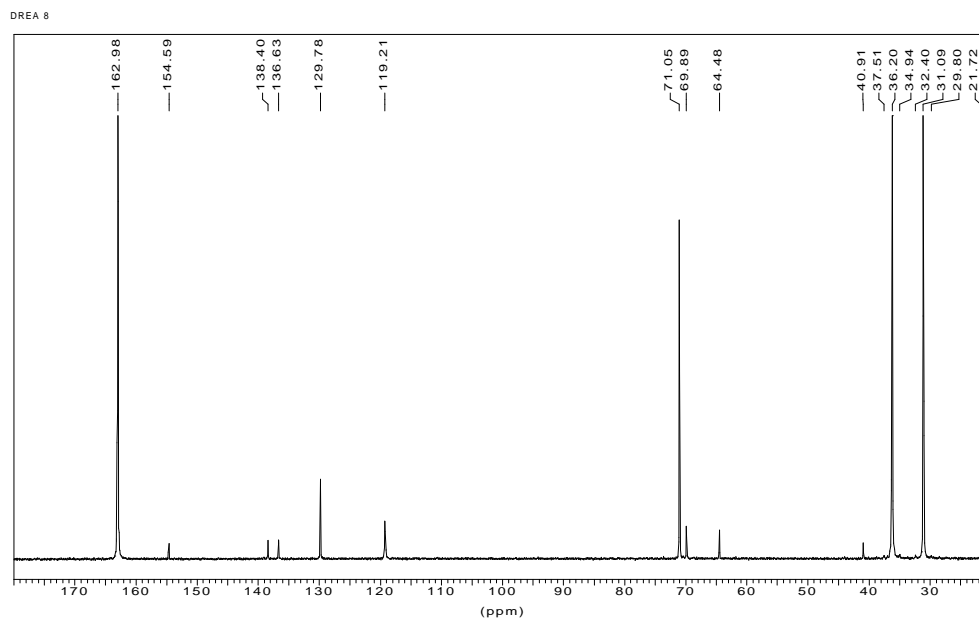


Figure 12. Proton decoupled ¹³C solution NMR spectrum of DREA8 – MDI/P600/DMPD (1.5/1.0/0.5).

3.1.7 DREA9 and DREA9R – MDI/P1000/DMPD (2.0/1.0/1.0)

The NMR spectra of samples DREA9 and DREA9R are shown in Figures 14 and 15 respectively. Sample DREA9R is a rerun of the synthesis of sample DREA9. The carbon chemical shifts are listed in Tables 2 and 4. The assignments of the unique carbons are shown in Figure 13. Differences in the spectra of DREA9 and DREA9R and DREA8 result from two factors. One is the difference in the molecular weights of the poly(ethylene glycol)s used in their preparation, 1000 for DREA9 and DREA9R versus 600 for DREA8, and the other is the ratio of the reactants used to prepare the polymers. Both affect the relative intensities of the resonances for the individual carbons in the polymers.

The resonance for carbon C₁₆ was difficult to observe in the proton decoupled spectra of DREA9 and DREA9R. The J-Mod spectrum of DREA9 is shown in Figure 16.

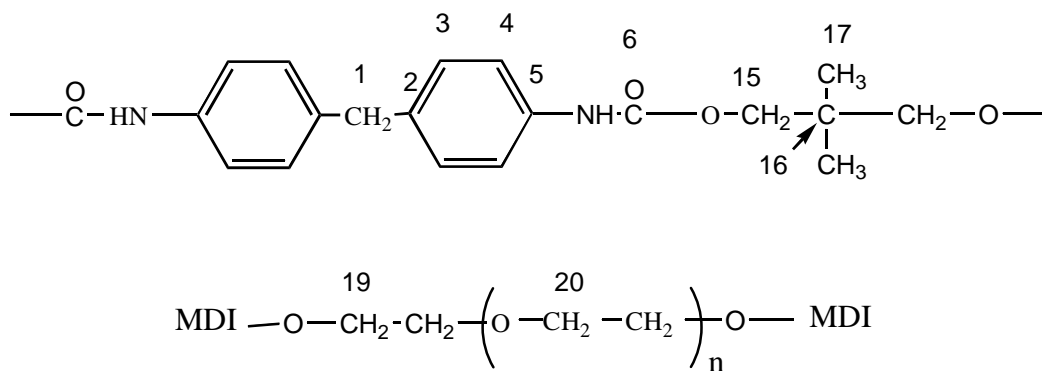


Figure 13. Structure and assignments of unique carbons in the hard (top) and soft (bottom) segments of poly(urethane)s DREA8, DREA9, DREA9R and DREA10.

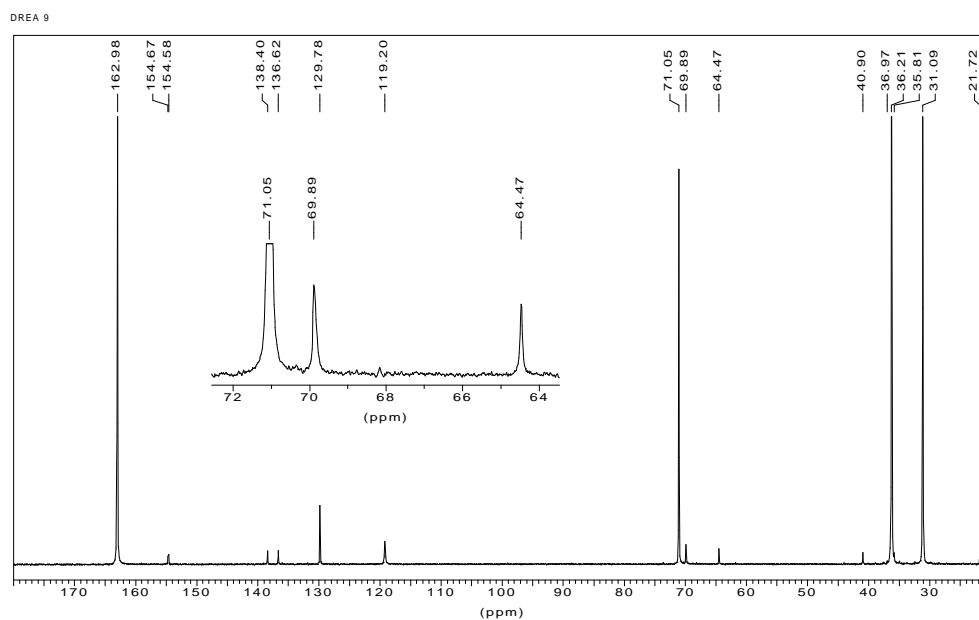


Figure 14. Proton decoupled ^{13}C solution NMR spectrum of DREA9 – MDI/P1000/DMPD (2.0/1.0/1.0).

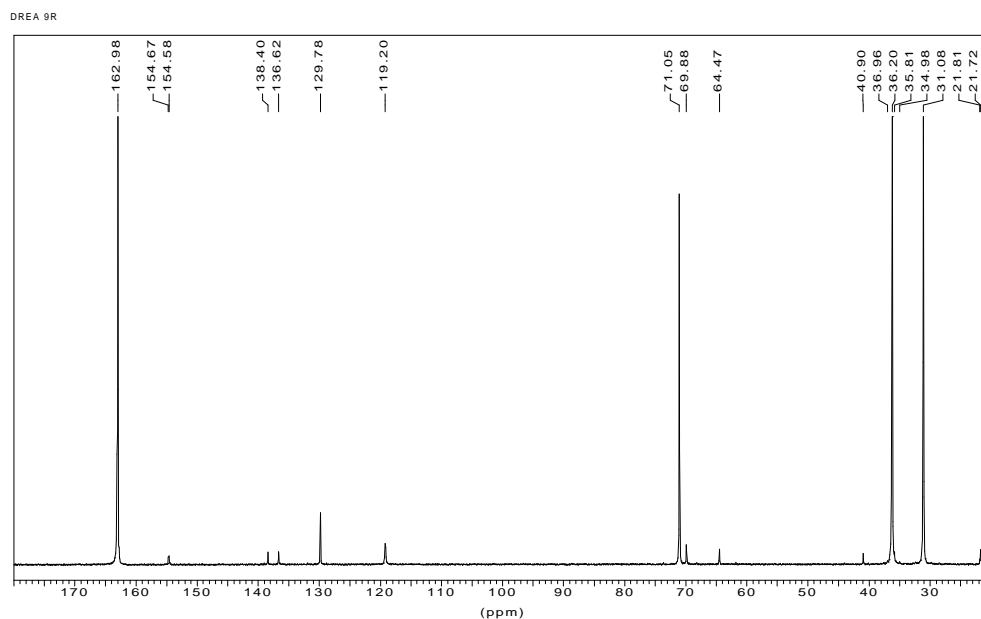


Figure 15. Proton decoupled ^{13}C solution NMR spectrum of DREA9R – MDI/P1000/DMPD (2.0/1.0/1.0).

A small negative resonance at ~35.8 ppm can be seen and is due to carbon C₁₆.

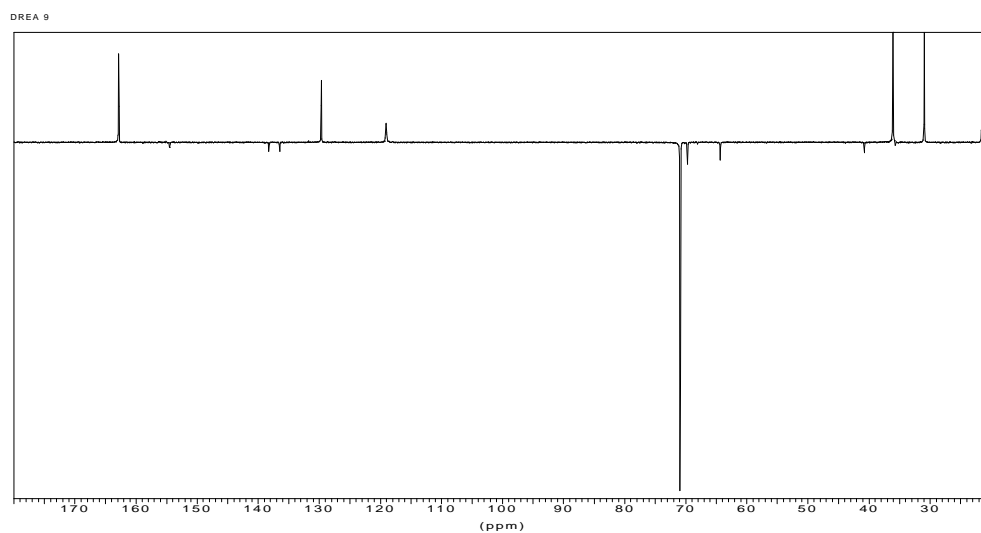


Figure 16. J-Mod spectrum of DREA9 – MDI/P1000/DMPD (2.0/1.0/1.0).

3.1.8 DREA10 – MDI/P1000/DMPD (6.0/1.0/5.0)

The spectrum of DREA10 is shown in Figure 17. The chemical shifts of the carbons are listed in Tables 2 and 4 and the assignment of the unique carbon resonances are shown in Figure 13. Comparing chemical shifts, the spectrum of DREA10 is similar to the spectra of DREA8, DREA9, and DREA9R. However, the intensity of the resonances for the carbons in the hard segment reflects the difference in the ratios of starting materials used to prepare these polymers. The resonance for carbon C₁₆ can be seen at 35.82 ppm.

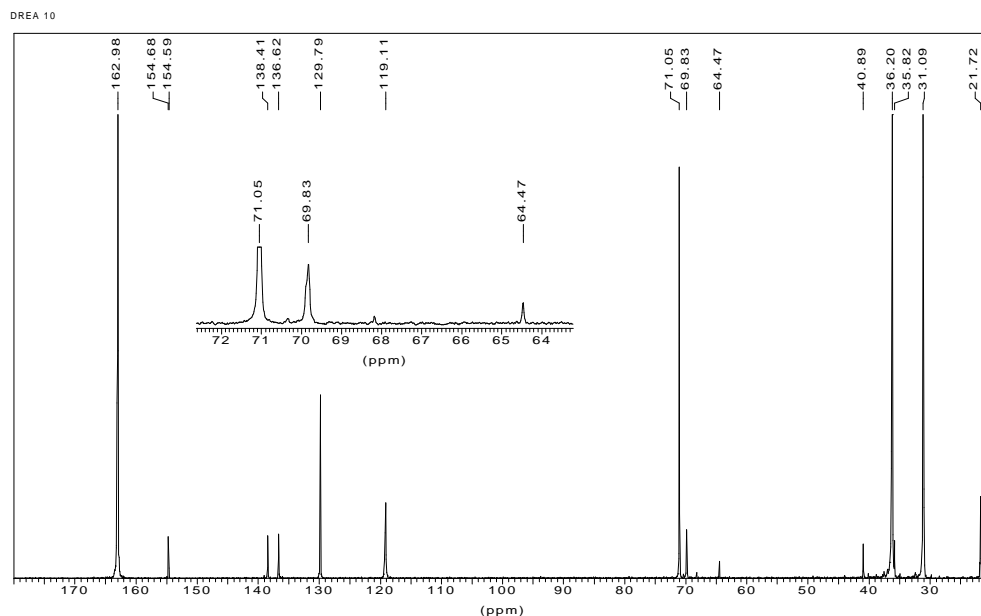


Figure 17. Proton decoupled ¹³C solution NMR spectrum of DREA10 – MDI/P1000/DMPD (6.0/1.0/5.0).

3.1.9 DREA13 and DREA13R – MDI/DEG (1/1)

The spectra of DREA13 and DREA13R are shown in Figures 18 and 19 respectively. The polymer contains no poly(ether glycol) and therefore has no soft segment. The carbon chemical shifts, assigned in the structures shown in Figure 20, are listed in Tables 2 and 4.

DREA13 and DREA13R have resonances at 73.51 ppm and 61.72 ppm that cannot be attributed to any of the carbon atoms in the top structure in Figure 20. Simulated spectra of MDI/DEG oligomers gave calculated chemical shifts for carbons C₂₃ and C₂₄ (bottom structure in Figure 20) of 72.6 ppm and 61.3 ppm respectively. On the basis of this simulation the resonances in DREA13 and DREA13R at 73.51 ppm and 61.72 ppm are attributed to terminal DEG carbons (C₂₃ and C₂₄ in Figure 20).

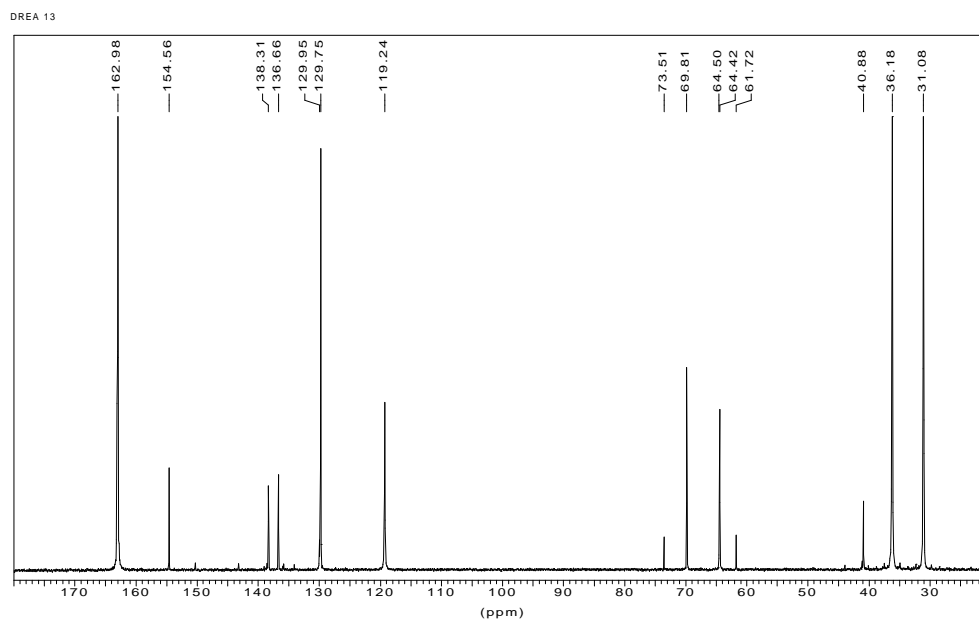


Figure18. Proton decoupled ^{13}C solution NMR spectrum of DREA13 – MDI/DEG (1.0/1.0).

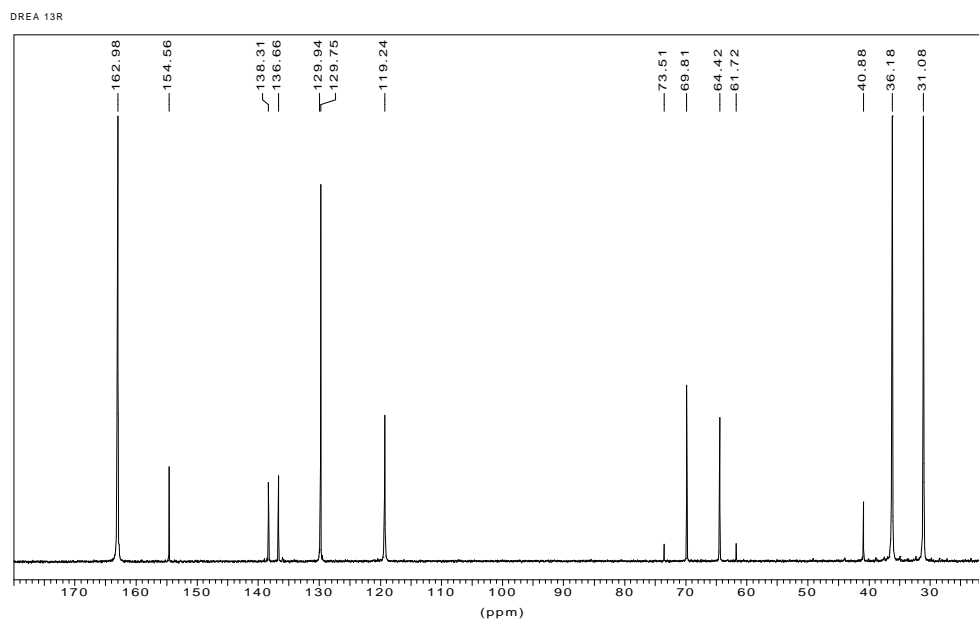


Figure 19. Proton decoupled ^{13}C solution NMR spectrum of DREA13R – MDI/DEG (1.0/1.0).

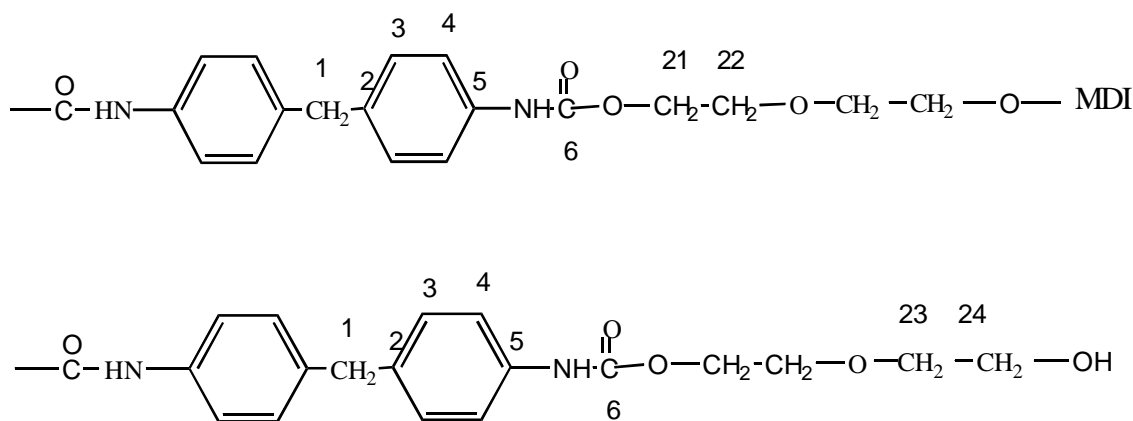


Figure 20. Structure and assignments of carbons for DREA13 and DREA13R.

3.1.10 DREA14 – MDI/T650/DMPD (6.0/1.0/5.0)

The spectrum of DREA14 is shown in Figure 21. The carbon chemical shifts are listed in Tables 2 and 3 and the assignments of the resonances are shown in Figure 7. This spectrum is similar to those for DREA3, DREA4, DREA5 and DREA6. Comparison of the spectra of DREA14 and DREA6 indicates that the resonances due to the poly(ether glycol) carbons are less intense for DREA14 than for DREA6. This is directly related to the molecular weights of the poly(ether glycol)s used to prepare the poly(urethane)s, that is, T650 (MW 650) for DREA14 and T1000 (MW 1000) for DREA6.

3.1.11 DREA16 and DREA16R – MDI/T1000 (1/1)

The spectra of DREA16 and DREA16R are shown in Figures 22 and 23 respectively. The carbon chemical shifts are listed in Tables 2 and 3 and the assignment of the unique carbon resonances are shown in Figure 7. This polymer is a poly(urethane) containing only soft segments.

A resonance at 62.10 ppm is also observed in the spectra of DREA16 and DREA16R. The spectrum of T1000 (poly(tetramethylene ether glycol)) is shown in Figure 24. This compound has resonances at 71.02 ppm, 27.16 ppm, 62.14 ppm, and 30.58 ppm. The first two correspond to carbons C_{13} and C_{14} in Figure 7 and the second two to the carbon adjacent to and one carbon removed from a terminal hydroxy group of this poly(ether glycol) respectively. On the basis of this evidence, the resonance at 62.10 ppm is attributed to the carbons with terminal hydroxyl groups.

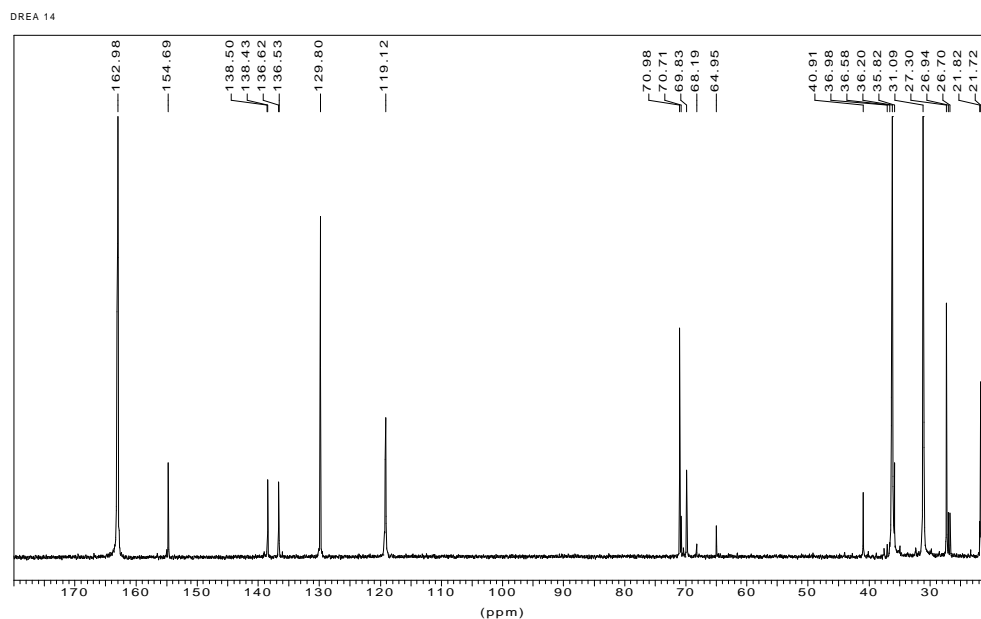


Figure 21. Proton decoupled ^{13}C solution NMR spectrum of DREA14 – MDI/T650/DMPD (6.0/1.0/5.0).

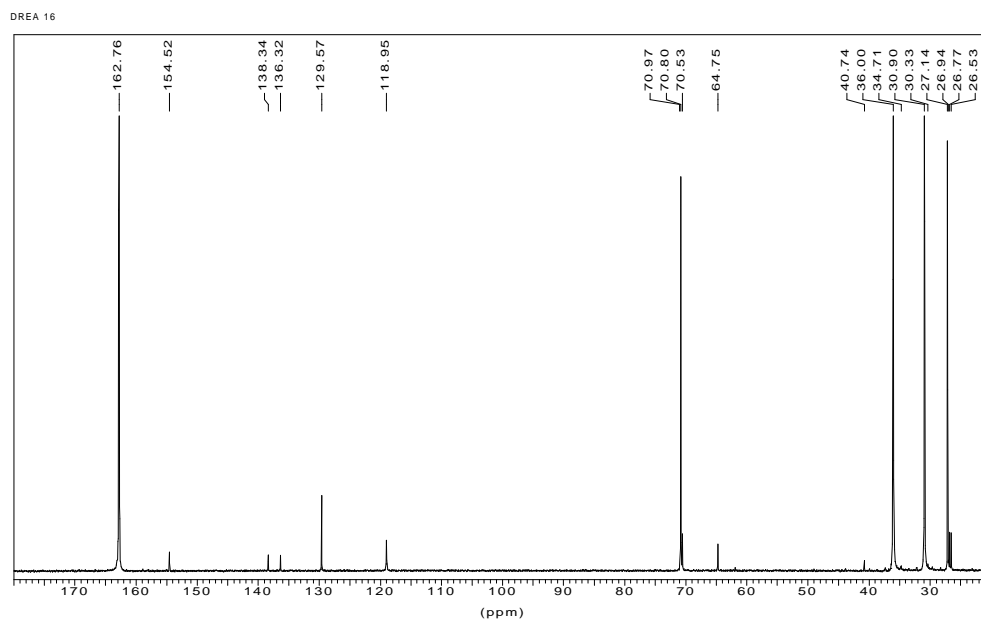


Figure 22. Proton decoupled ^{13}C solution NMR spectrum of DREA16 – MDI/T1000 (1.0/1.0).

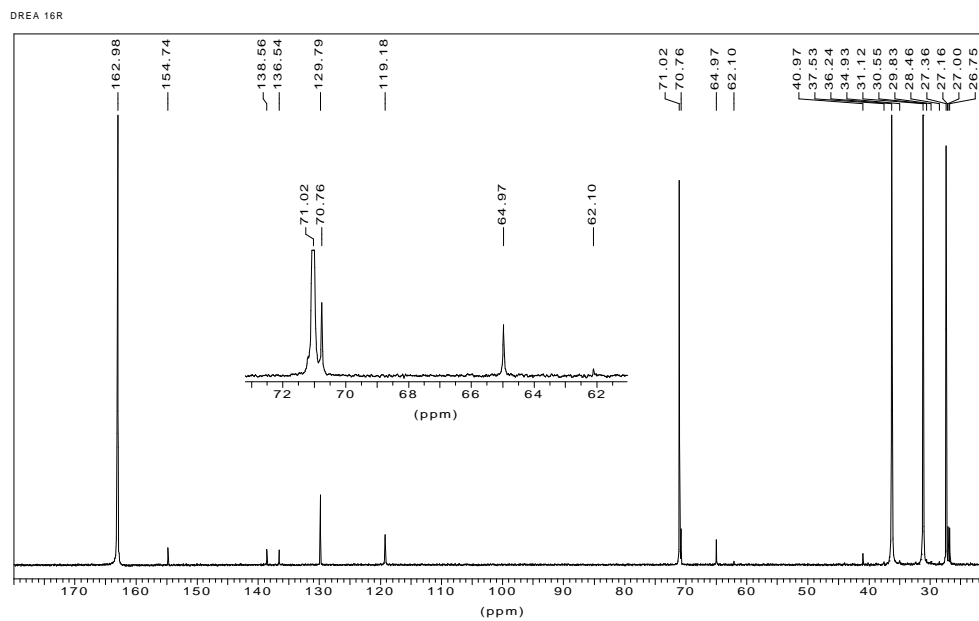


Figure 23. Proton decoupled ^{13}C solution NMR spectrum of DREA16R – MDI/T1000 (1.0/1.0).

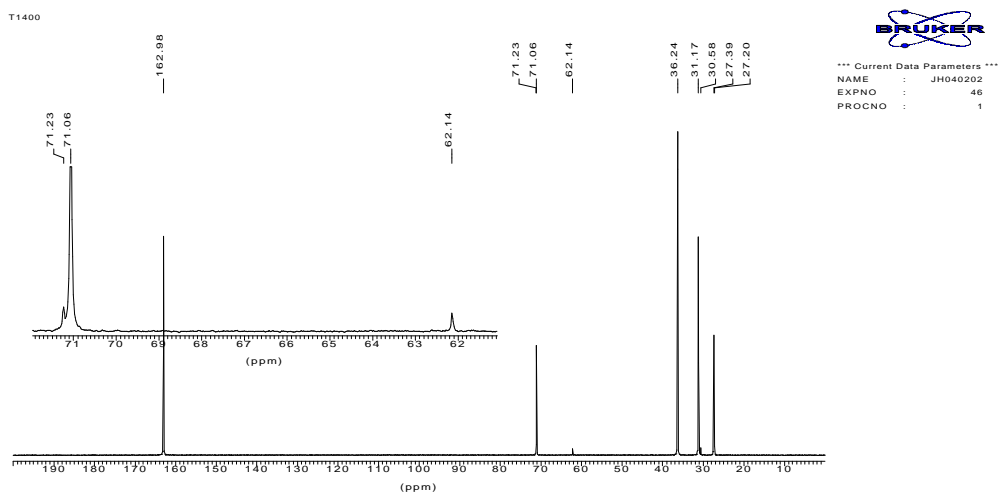


Figure 24. Proton decoupled ^{13}C solution NMR spectrum of T1000.

3.1.12 DREA17 – MDI/T1000/DMPD (4/1/3)

The spectrum of DREA17 is shown in Figure 25. The carbon chemical shifts are listed in Tables 2 and 3 and the assignments of the unique carbons are shown in Figure 7. The spectrum of DREA17 is similar to the spectra for DREA3, DREA4, DREA5, DREA6, and DREA14. As all are MDI/poly(tetramethylene ether glycol)/DMPD poly(urethane)s this would be expected.

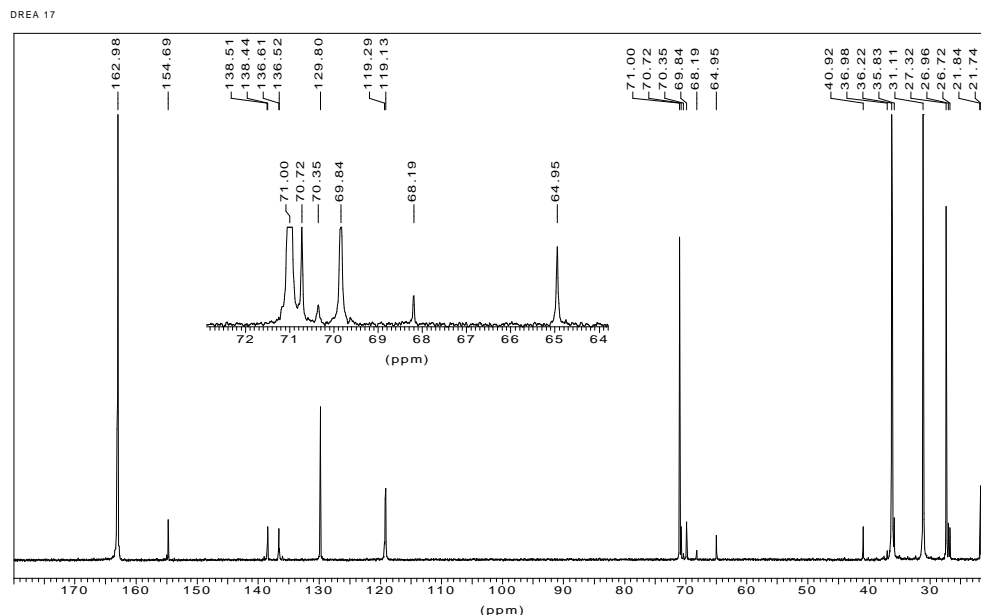


Figure 25. Proton decoupled ^{13}C solution NMR spectrum of DREA 17 – MDI/T1000/DMPD (4/1/3).

3.2 HDI Based Poly(urethane)s

3.2.1 DREA7 HDI/DMPD/DEG (2.0/1.0/1.0)

The spectrum of DREA7 is shown in Figure 26. The chemical shifts of the unique carbons in this polymer are listed in Tables 5 and 6. The assignments of the unique carbons are shown in Figure 27. DREA7 is prepared using two diols, 2,2-dimethyl-1,3-propanediol and diethylene glycol, but contains no poly(ether glycol) and therefore is not a block copolymer.

DREA7 has four resonances arising from the HDI portion of the polymer. Three of these, at 41.32 ppm, 30.56 ppm, and 27.10 ppm, are due to the three unique methylene carbons in the HDI portion of the polymer, and the other is due to the urethane carbonyl carbon.

The resonances for the DMPD and PEG portions of the polymer are similar to those for the MDI based poly(urethane)s containing these diols. For instance, the chemical shifts of C_{8H} (69.60 ppm), C_{9H} (35.85 ppm) and C_{10H} (21.75) for DREA7 are very similar to the chemical shifts of C₁₅ (69.84 ppm), C₁₆ (35.83 ppm), and C₁₇ (21.77 ppm) for DREA4. The spectrum of DREA7 has a resonance at 68.25 ppm. This is similar to the MDI-based poly(urethane)s containing DMPD. This resonance is attributed to a terminal DMPD hydroxyl substituted carbon.

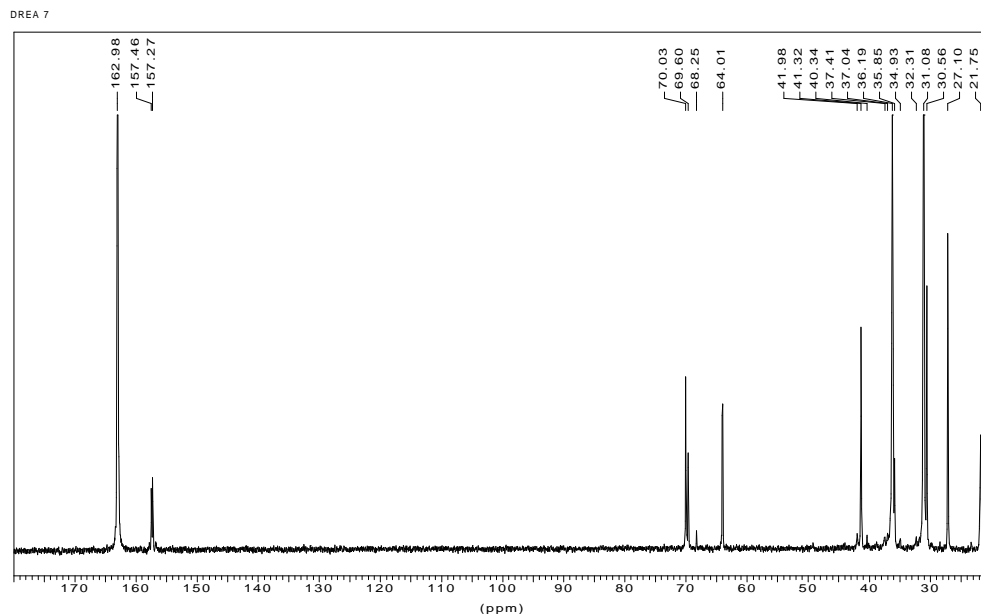


Figure 26. Proton decoupled ¹³C solution NMR spectrum of DREA7 – HDI/DMPD/PEG (2/1/1).

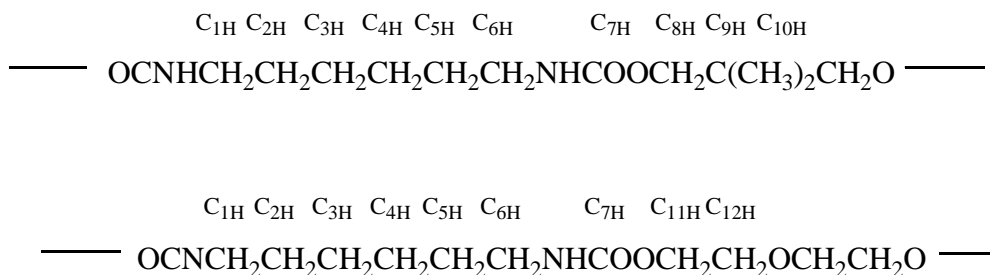


Figure 27. Structure and assignments of carbons for DREA7.

3.2.2 DREA11 – HDI/P1000/DMPD (6.0/1.0/5.0)

The spectrum of DREA11 is shown in Figure 28. The chemical shifts of the unique carbons are listed in Tables 5 and 6 and the assignments of the carbons are shown in Figure 29.

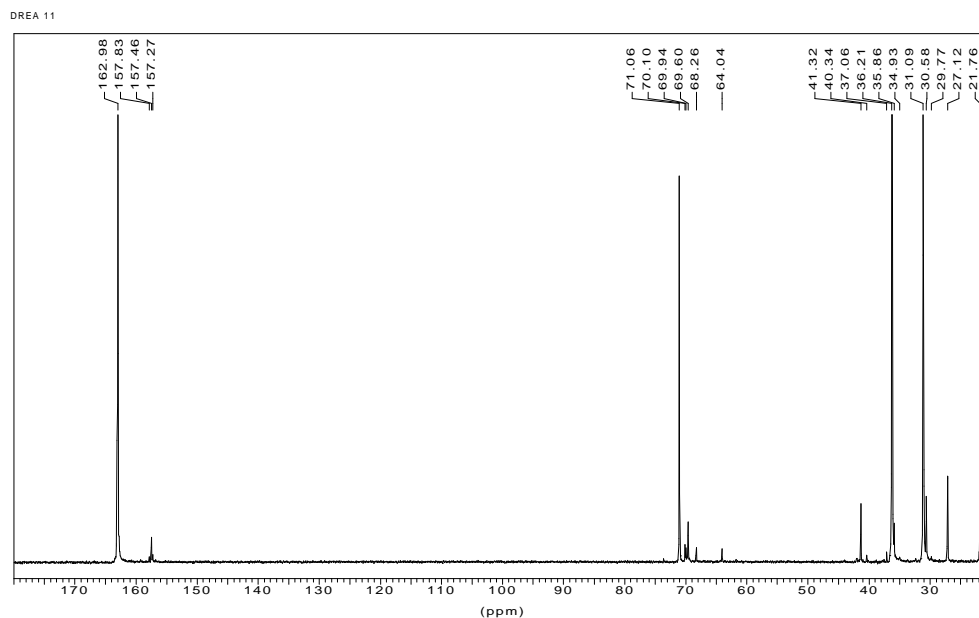


Figure 28. Proton decoupled ^{13}C solution NMR spectrum of DREA11 – HDI/P1000/DMPD (6/1/5).

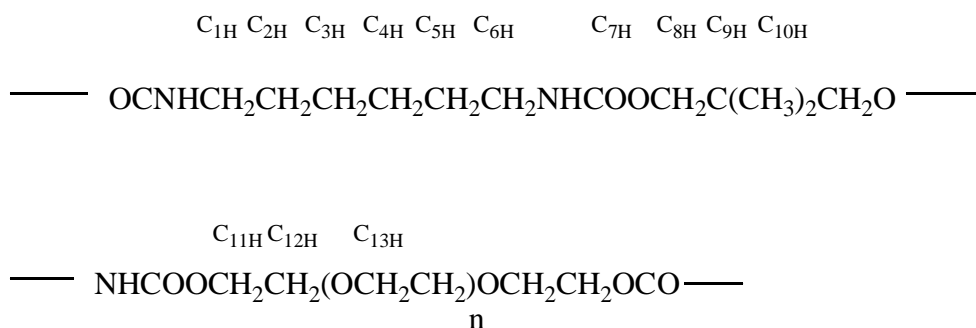


Figure 29. Structure and assignments of carbons for DREA11.

This poly(urethane) differs from DREA7 in that it contains a poly(ether glycol), P1000, and therefore is a block copolymer. There are three resonances arising from the unique carbons in the P1000 portion of the polymer. They are denoted as $\text{C}_{11\text{H}}$, $\text{C}_{12\text{H}}$, and $\text{C}_{13\text{H}}$. The chemical shifts of the carbons closest to the urethane carbonyl carbon are similar to the chemical shifts

of the carbons arising from the diethylene glycol portion of DREA7. Comparison of the chemical environments of these carbons in DREA7 and DREA11 indicates that they are very similar.

3.2.3 DREA18 - HDI/T1000/DMPD (4.0/1.0/3.0)

The spectrum of DREA18 is shown in Figure 30. The chemical shifts of the unique carbons are listed in Tables 5 and 6 and the assignments of the carbons are shown in Figure 31.

The chemical shifts of the HDI/DMPD portion of this polymer are similar to those for DREA11. The chemical shifts of the T1000 portion of this polymer are similar to those for the MDI based polymers containing a poly(tetramethylene ether glycol). Six distinct carbons arising from the T1000 portion of the polymer, C_{14H} through C_{19H}, can be seen in the spectrum.

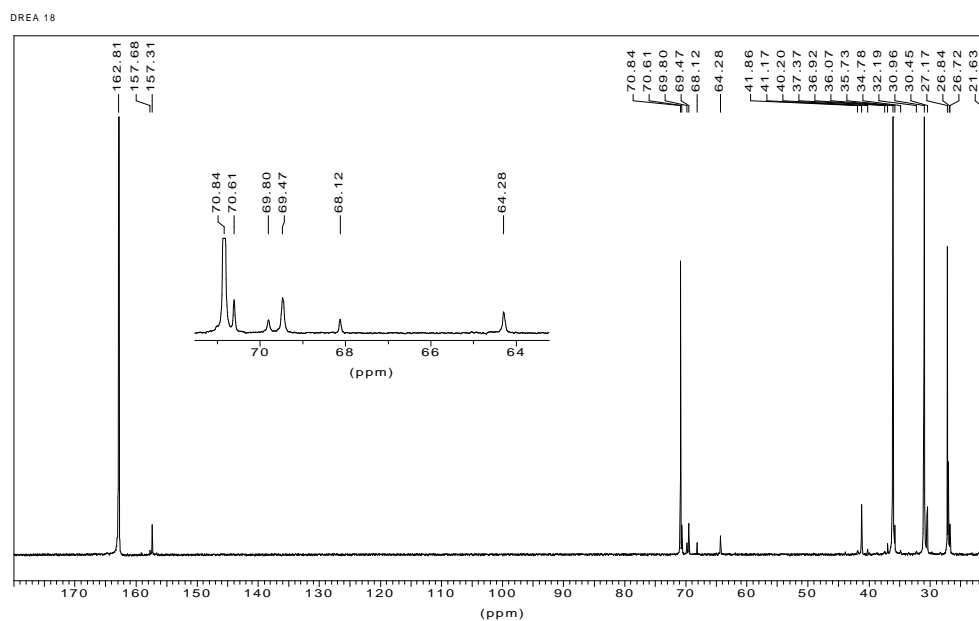


Figure 30. Proton decoupled ¹³C solution NMR spectrum of DREA18 – HDI/T1000/DMPD (4/1/3).

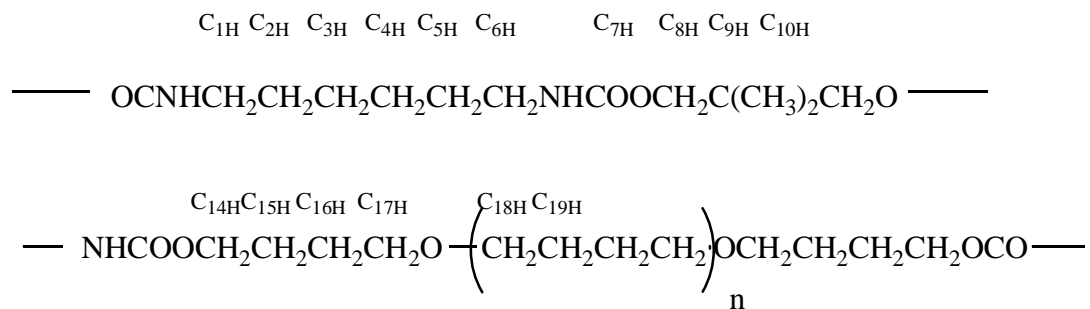


Figure 31. Structure and assignments of carbons for DREA18.

4. Conclusions

The solution ^{13}C NMR spectra of 15 thermoplastic poly(urethane) have been presented. The chemical shifts of the unique carbons in each of the poly(urethane)s have been assigned and can be used to differentiate between urethanes synthesized from one of two diisocyanates, either MDI or HDI, one of three diols, either butanediol, 2,2-dimethyl-1,3-propanediol or diethylene glycol, and one of two poly(ether glycol)s, either poly(tetramethylene ether glycol) or poly(ethylene glycol). In addition the chemical shift data can be used to determine if the poly(urethane) is a block copolymer or contains only urethane rich or poly(ether glycol) rich segments.

Terminal hydroxyl carbons can be identified in the spectra of several poly(urethane)s containing DMPD. The intensity of the resonance at ~ 68.20 ppm depended on the ratio of reactants used in the preparation of the polymer. That is, as the ratio of DMPD to poly(ether glycol) increased, the resonance at 68.20 ppm increased in intensity. Terminal hydroxyl carbons were also observed for DREA13 and DREA13R. These polymers were synthesized from MDI/DEG (1/1). The intensity of these resonances, under the right experimental conditions, may provide a way to compare the molecular weights of different batches of a particular poly(urethane).

5. References

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4. David Porter, **Group Interaction Modelling of Polymer Properties**, Marcel Dekker, Inc., New York (1995).
5. D. W. Van Krevelen, **Properties of Polymers, Third Edition**, Elsevier, New York (1997).
6. D. Cook, "Phase Mixed Polyurethane Synthesis", DREA Contractor Report 2000-076, July 2000.

Table 2. Chemical shifts of carbons C1 through C6 in MDI based poly(urethane)s. C₁, C₂ etc. refer to carbons in Figures 4, 7, 13, and 20.

SAMPLE	CHEMICAL SHIFT (PPM)					
DREA	C₁	C₂	C₃	C₄	C₅	C₆
1	40.89	136.61	129.76	119.19	138.43	154.69
1R	40.90	136.61	129.75	119.20	138.43	154.69
3	40.96	136.54	129.79	119.18	138.55	154.74
4	40.91	136.62	129.80	119.13	138.44	154.69
5	40.79	136.38	129.63	118.99	138.40	154.55
6	40.91	136.62	129.81	119.13	138.45	154.69
8	40.91	136.63	129.78	119.21	138.40	154.59
9	40.90	136.62	129.78	119.20	138.40	154.58
9R	40.90	136.62	129.78	119.20	138.40	154.58
10	40.89	136.62	129.79	119.11	138.41	154.59
13	40.88	136.66	129.75	119.24	138.41	154.56
13R	40.88	136.66	129.75	119.24	138.31	154.56
14	40.91	136.53	129.80	119.12	138.43	154.69
16	40.74	136.32	129.57	118.95	138.34	154.52
16R	40.97	136.54	129.76	119.18	138.56	154.74
17	40.92	136.52	129.80	119.13	138.44	154.69

Table 3. Chemical shifts of carbons C₇ through C₁₈ in MDI/poly(tetramethylene ether glycol) based poly(urethane)s. C₇, C₈, etc. refer to carbons in Figures 4 and 7.

SAMPLE	CHEMICAL SHIFTS (PPM)											
	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈
1	64.70	26.33										
1R	64.70	26.33										
3			64.97	26.75	27.00	70.76	71.02	27.36	69.87		21.77	68.21
4			64.95	26.72	26.96	70.72	70.99	27.32	69.84	35.83	21.74	68.20
5			64.80	26.59	26.84	70.60	70.87	27.20	69.70	35.71	21.62	
6			64.95	26.72	26.96	70.73	71.00	27.33	69.84	35.84	21.74	
14			64.95				70.98	27.30	69.83	35.82	21.72	
16			64.75	26.53			70.97	27.14				
16R			64.97	26.75			71.02	27.36				
17			64.95	26.72			71.00	27.32	69.84	35.83	21.74	

Table 4. Chemical shifts of carbons C₁₅ through C₂₄ in MDI/poly(ethylene glycol) and MDI/PEG based poly(urethane)s. C₁₅, C₁₆, etc. refer to carbons in Figures 13 and 20.

SAMPLE	CHEMICAL SHIFTS (PPM)									
	C ₁₅	C ₁₇	C ₁₇	C ₁₈	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄
8	69.89		21.72		64.48	71.05				
9	69.89		21.72		64.47	71.05				
9R	69.88		21.72		64.47	71.05				
10	69.83	35.82	21.72	68.20	64.47	71.05				
13							64.50	69.81	73.51	61.72
13R							64.42	69.81	73.51	61.72

Table 5. Chemical shifts of carbons C_{1H} through C_{7H} for HDI based poly(urethane)s. C_{1H} , C_{2H} etc. refer to carbons in Figures 27,29, and 31.

SAMPLE	CHEMICAL SHIFTS (PPM)						
	C_{1H}	C_{2H}	C_{3H}	C_{4H}	C_{5H}	C_{6H}	C_{7H}
DREA7	41.32	30.56	27.10	27.10	30.56	41.32	157.30
DREA11	41.32	30.58	27.12	27.12	30.58	41.17	157.46
DREA18	41.17	30.45	26.84	26.84	30.45	41.17	157.31

Table 6. Chemical shifts of carbons C_{8H} through C_{19H} for HDI based poly(urethane)s. C_{8H} , C_{9H} etc. refer to carbons in Figures 27,29, and 31.

SAMPLE	CHEMICAL SHIFTS (PPM)											
	C_{8H}	C_{9H}	C_{10H}	C_{11H}	C_{12H}	C_{13H}	C_{14H}	C_{15H}	C_{16H}	C_{17H}	C_{18H}	C_{19H}
DREA7	69.60	35.85	21.75	64.01	70.03							
DREA11	69.60	35.86	21.76	64.04	70.10	71.06						
DREA18	69.47	35.73	21.63				64.28	26.72	26.84	70.61	70.84	27.17

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The ^{13}C solution nuclear magnetic resonance (NMR) spectra of the 15 poly(ether)urethanes are presented. The poly(urethane)s were prepared using one of two diisocyanates, either methylene diphenyl diisocyanate (MDI) or hexamethylene diisocyanate (HDI), one of five poly(ether glycol)s, poly(tetramethylene ether glycol) of molecular weight 650, 1000, or 1400, or poly(ethylene glycol) of molecular weight 600 or 1000, and one of three chain extenders, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, or diethylene glycol. These polymers were prepared as part of a modelling study to determine if Group Contribution Theory and Group Interaction Modelling could be used to predict dynamic mechanical properties of poly(ether)urethanes on the basis of the structural fragments in the polymers.

The chemical shifts of the unique carbons in each of the poly(urethane)s are assigned. They can be used to unambiguously identify the diisocyanate/diol/poly(ether glycol) used to prepare the various polyurethanes. For some compounds the spectra show resonances for terminal hydroxyl substituted carbons. These could provide a method, under the right experimental conditions, to compare molecular weights of batches of the same polymer.

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Solution ^{13}C NMR
Chemical shifts
poly(ether)urethanes
4,4'-methylene bis(phenyl isocyanate) (MDI)
1,6-diisocyanatohexane (HDI)
Poly(tetramethylene ether glycol)s
Poly(ethylene glycol)
2,2-dimethyl-1,3-propanediol (DMPD)
diethylene glycol
1,4-butanediol

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